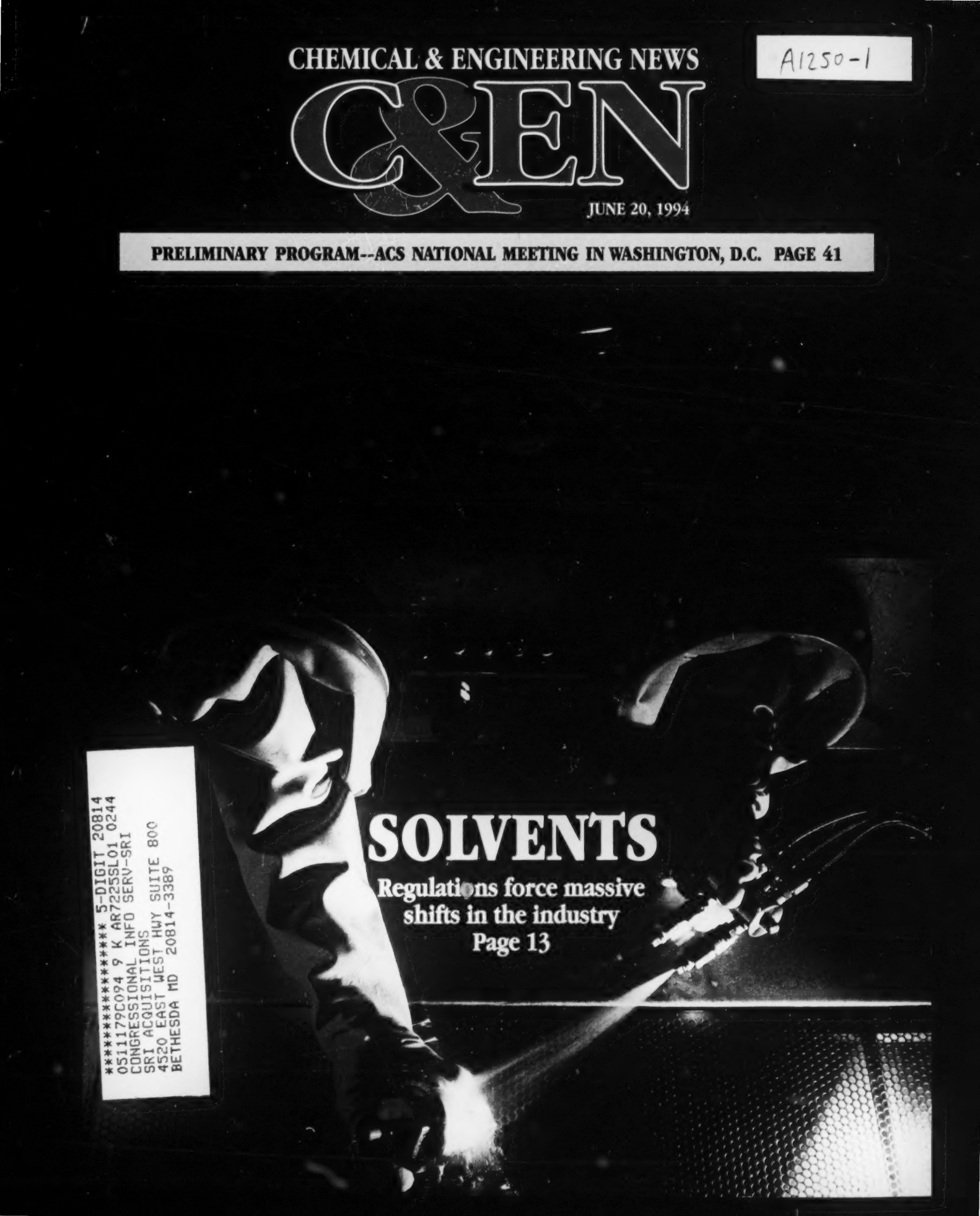
A1250-1

CHEMICAL & ENGINEERING NEWS

C&EN

JUNE 20, 1994

PRELIMINARY PROGRAM--ACS NATIONAL MEETING IN WASHINGTON, D.C. PAGE 41



SOLVENTS

Regulations force massive shifts in the industry

Page 13

**********5-DIGIT 20814
05111179C094 9 K AR7225SL01 0244
CONGRESSIONAL INFO SERV-SRI
SRI ACQUISITIONS
4520 EAST WEST HWY SUITE 800
BETHESDA MD 20814-3389

CHEMICAL & ENGINEERING NEWS

C&EN

JUNE 20, 1994

NEWS OF THE WEEK

■ After months of interagency debate, Congress gets draft legislation for implementing chemical weapons treaty and holds a public hearing on ratification. **Page 6**

■ In a development that represents a step toward the design of molecular electronic devices, researchers have made conducting filaments of polyaniline on a nanometer scale. **Page 7**

■ Merck, the world's largest drug maker, names Raymond V. Gilmartin—an outsider with no pharmaceutical experience—as new president and chief executive after an 18-month search. **Page 8**

■ Dow may consider bankruptcy option in the future if too many women opt out of proposed $4.2 billion settlement plan for silicone breast implants and pursue individual lawsuits. **Page 8**

■ A jury finds that Exxon's reckless conduct caused the *Exxon Valdez* oil spill; damages of up to $16.5 billion may be claimed. **Page 8**

■ Several research groups have purified, characterized, and cloned the blood platelet regulatory factor thrombopoietin; results have potential implications for cancer chemotherapy. **Page 9**

COVER: Lab worker tests new solvent for cleaning metal parts. Photo courtesy of Union Camp

Volume 72, Number 25
CENEAR 72 (25) 1–88
ISSN 0009-2347

GOVERNMENT

Chemical companies in West Virginia's Kanawha Valley make public their worst case accident scenarios, informing the public how serious accidental releases could be and what the companies are doing to prevent them. **Page 22**

Congress receives policy statements from ACS on education issues, research funding, EPA's research budget, and the Administration's proposal to review the use of chlorinated compounds. **Page 26**

SCIENCE/TECHNOLOGY

German abstracting service specializing in chemical engineering fields, a joint venture of Bayer and BASF, boasts of stringent selection process and seeks to broaden subscriber base. **Page 30**

New process achieves 90% conversion of crude butadiene to styrene in two steps—cyclodimerization and oxidation—at potentially lower cost than conventional methods. **Page 31**

ACS NEWS

Proposals for increasing minority participation in chemical sciences and ACS result from recent ACS Board retreat. **Page 38**

PRELIMINARY PROGRAM

ACS's 208th national meeting in Washington, D.C., in August offers a broad range of technical sessions and activities; listing and highlights of symposia are included along with full general program and registration form. **Page 41**

BUSINESS

Organic solvents—being phased out of many products and industrial processes because of federal regulations addressing health and the environment—are being replaced by aqueous formulations, small-volume organics, and no-solvent technologies. Page 13

LETTERS 4
EDITOR'S PAGE 5
CONCENTRATES
Business 11
Government 21
Science/Technology 28
THE DEPARTMENTS
Software/Database Update 32
ACS Comment 35
Meetings 87
Newscripts 88

Chemical & Engineering News
1155—16th St., N.W., Washington, D.C. 20036
Editor: Michael Heylin (202) 872-4501
Managing Editor: Madeleine Jacobs
Assistant Managing Editors: James H. Krieger, Janice R. Long, Rebecca L. Rawls, Donald J. Soisson, William J. Storck
Staff Editor: Ernest L. Carpenter
Senior Correspondents: Lois R. Ember, Wilbert C. Lepkowski
News Editor: Richard J. Seltzer
Senior Editors: Northeast News Bureau: Marc S. Reisch, Stephen C. Stinson; Chicago: Joseph Haggin; Washington: Stuart A. Borman, Mairin B. Brennan, Doron Dagani, Bette Hileman, Pamela S. Zurer
Associate Editors: Jane K. Baker, Robin M. Giroux
Service Departments Editor: Linda Romaine Ross
Editing Services: Arlene Goldberg-Gist (Head), Rita E. Johnson (Editorial Assistant), Patricia Oates (Administrative Assistant)
News Bureaus: Northeast: (908) 906-8300 Ann M. Thayer (Head), Elisabeth Kirschner (Assistant Editor), Rachel Eskenazi (Administrative Assistant). Houston: (713) 558-2912 Susan J. Ainsworth (Head). Washington: (202) 872-4495 David J. Hanson (Head), Raymond A. Goodlett (Intern). West Coast: (510) 653-3630 Rudy M. Baum (Head), (206) 517-5034 Deborah L. Illman (Associate Editor) **Foreign Bureau:** London: (01) 4481 870-6884 Patricia L. Layman (Senior Editor)
Graphics and Production: Leroy Corcoran (Head). Barbara Fryer (Art Director). Linda Mattingly (Staff Artist). Diane Kelly (Costing)
Composition Systems Administrator: Vincent L. Parker. **Assistant:** Robin L. Braverman
Business Manager: Arthur Poulos
Marketing Manager: David Schulbaum
Circulation Manager: Donna W. Carvana
ADVISORY BOARD: Marvin Cassman, Jerry Caulder, P. M. Chakrabarti, Rhetta Q. Davis, Peter B. Dervan, Marye Anne Fox, Richard A. Lerner, Gerald Epstein, Stephen J. Lippard, Peter J. Neff, James N. Pitts Jr., Douglas J. Raber, Bassam Z. Shakhashiri, Harold A. Sorgenti, Kathleen C. Taylor, Margaret A. Tolbert, Charles S. Tuesday, Theodore R. Williams
Published by
AMERICAN CHEMICAL SOCIETY
(202) 872-4600; TDD (202) 872-4432
John Kistler Crum, Executive Director
Robert H. Marks, Director, Publications Division
PUBLISHING BOARD: Joseph A. Dixon *(Chairman); Board of Directors Chairman:* Paul H. L. Walter, *President:* Ned D. Heindel; Paul S. Anderson, Richard L. Deming, Paul W. Jennings, Barbara J. Peterson
Subscription & Member Record Service: Send all new and renewal subscriptions with payments to: ACS, Dept. L-0011, Columbus, Ohio 43268-0011. Correspondence and telephone calls for changes of address, claims for missing issues, subscription orders, status of records and accounts should be directed to: Manager, Member & Subscriber Services, ACS, P.O. Box 3337, Columbus, Ohio 43210; (800) 333-9511 or (614) 447-3776.

For changes of address, include both old and new addresses with ZIP code numbers and mailing label from a recent issue. Allow four weeks for change to become effective. Claims for missing numbers will not be allowed if loss was due to failure of notice of change of address to be received in the time specified; if claim is dated (a) North America: more than 90 days beyond issue date, (b) all other foreign: more than one year beyond issue date; or if the reason given is "missing from files."

Subscription Rates 1994: Printed editions: nonmembers U.S. 1 yr. $115, 2 yr. $207; outside U.S. 1 yr. $152, 2 yr. $281. Air freight rates available on request. Rates above do not apply to nonmember subscribers in Japan, who must enter subscription orders with Maruzen Co. Ltd., 3–10 Nihonbashi 2-chome, Chuo-ku, Tokyo 103, Japan. Tel: (03) 272-7211. Single copies: Current $18. Rates for back issues and volumes are available from Microforms & Back Issues Office, ACS, 1155—16th St., N.W., Washington, D.C. 20036. Back and current issues available on microfilm and microfiche. Rates on request from Microform Program, ACS.

Chemical & Engineering News (ISSN 0009-2347) is published weekly except for the last week in December by the American Chemical Society at 1155—16th St., N.W., Washington, D.C. 20036. Second-class postage paid at Washington, D.C., and additional mailing offices. POSTMASTER: Send address changes to C&EN, Member & Subscriber Services, P.O. Box 3337, Columbus, Ohio 43210. ACS assumes no responsibility for the statements and opinions advanced by the contributors to its publications.

Advertising Management: CENTCOM LTD.
(For list of offices see page 87)
Office of Ombudsman: (800) ACS-5558, No. 5–4
© Copyright 1994, American Chemical Society
Canadian GST Reg. No. R127571347

LETTERS

Chemical calculator is here

Stu Borman, in his article "Handheld Chemical Calculator Is On Its Way" (C&EN, May 16, page 50), makes this new computer program (O. Bertrand Ramsay's program is not yet available in handheld calculator format) appear revolutionary. Indeed, it does appear to have many features that sound fresh, but the idea of a chemical calculator is not new. For the past couple of years, I have been using a commercial handheld calculator, the HP 48SX Scientific Expandable, which I would liken to the program Ramsay has been developing. Borman's unawareness of this calculator surprises me: College students all across the country are quite conscious of its existence.

This calculator, without accessories, allows calculations with units, does unit conversions for almost every imaginable unit, and solves mathematical equations. In addition, accessory cards are available for various uses. The HP Solve Equation Library accessory card is certainly a rival to Ramsay's program. This accessory card contains a wealth of chemical and engineering information. There is a library of chemical and engineering equations that displays not only equations, but also graphically demonstrates variables and their use. There is a table of chemical and engineering constants. This accessory card also contains a periodic table of the elements with a database of the properties of each element. These properties can even be viewed graphically as a function of atomic number.

With the accessory card installed, I can type in chemical formulas and, with the touch of a key, have the formula weight. Useful equations are selected from the various menus, variables input, constants automatically imported, and the equation solved. Because this is a versatile calculator and not dedicated to a single purpose, one can also carry out statistical analyses, graph data, calculate loan payments, keep track of appointments, or look up an associate's telephone number and address.

This calculator allows development of programs and libraries to take place on a personal computer. The programs and data are then downloaded to the calculator or stored on removable RAM cards. The HP 48SX's versatility and expandability make it every bit as useful as the program under development by Ramsay. The chemical calculator is not on its way, it's already here.

Douglas E. Wedman
Los Alamos National Laboratory
Los Alamos, N.M.

No respect

In her letter, "Respect for interviewees" (C&EN, May 30, page 2), Kathryn A. Hemker makes a very important point about an issue that is truly an embarrassment to the chemical profession. My personal experience perfectly supports her case relating the "deplorable treatment" that her husband received as an interviewee for academic and industrial positions in chemistry.

In early 1991, a certain large U.S. chemical company invited me for an interview about one-half year after I had initially inquired by mail about the potential of obtaining a research position with them. I took a day of vacation from my job in Canada and flew there for the interview. The whole process went extremely well, and when I left, I was almost offered a position. I was told that only a few formalities needed to get ironed out.

More than three months passed and I heard not a word from the company. I finally decided to phone and inquire about the fate of my application. A very feeble apology for the delay was followed by news that the funding for the position for which I was interviewed did not materialize. Why did they fly me down there if they were not certain that a scientific position was available?

Luckily, I had a reasonable chemistry job at that time in Canada and consequently I was not very bothered by the outcome. What did amaze and shock me was exactly what Hemker describes so well in her letter—the total lack of respect that was shown toward me by the representatives of the very highly respected chemical company that had interviewed me.

Incidents of this sort are a sad reflection of the acute deficiency of humanistic thinking that exists among today's technical leaders, and that is perhaps most evident in the chemical world.

Walter V. Cicha
Newark, Del.

Authorization to photocopy any article for internal or personal use beyond the fair use provisions of the Copyright Act is granted by ACS to libraries and other users registered with the Copyright Clearance Center (CCC), provided that the fee of $3.00 per article copy is paid directly to CCC, 222 Rosewood Dr., Danvers, Mass. 01923, USA. Copying for other than internal or personal use without express permission of ACS is prohibited. Address requests for customized bulk reprints to ACS Copyright Administrator, 1155—16th St., N.W., Washington, D.C. 20036, or call (202) 872-4367. The CCC Code for C&EN is 0009-2347/94 $3.00.

Environment, Health Concerns Force Shift In Use Of Organic Solvents

■ ***Federal regulations favor aqueous formulations, as well as no-solvent technologies and small-volume alternative organics***

Elisabeth M. Kirschner,
C&EN Northeast News Bureau

Petroleum photo

Technician evaluates CFC alternative for cleaning electronic parts.

Once the medium of choice for organic chemistry, many organic solvents are being phased out of products and processes for environmental and health reasons. Historically, solvents have been used to mobilize solids, preparing them for reactions; to carry particles onto surfaces in coatings, then evaporate; and to clean parts and equipment by separating grease and grime and carrying them away.

Industry is minimizing or eliminating solvents to cut hazardous waste costs as well as Toxics Release Inventory (TRI) chemical emissions, as mandated under the federal Superfund law. Many companies are turning to aqueous carriers or high-solid contents in paints and coatings, and to hot-melt, ultraviolet-cured, and waterborne adhesives. In the cosmetics and personal care markets, solvents have been dropped from some formulations because of concerns about volatile organic compounds (VOCs). Water-based hairsprays and solid deodorant sticks have grabbed market share.

As solvent use continues its slow overall decline, demand for some solvents is shifting. Large-use chemicals that could dissolve seemingly anything—such as acetone, 1,1,1-trichloroethane, and xylene—are being replaced by myriad high-value specialty chemicals, each grabbing small niches. Such solvent replacements as aqueous-compatible organic solvents and nonsolvent technologies are enjoying growth.

The solvent market is dominated by Shell, Union Carbide, Exxon, Dow Chemical, and Eastman Chemical. According to industry consultant Freedonia Group, Cleveland, these companies accounted for 53% of U.S. solvent sales in 1992. Sales of the nearly $3 billion solvent industry are forecast to grow a sluggish 0.8% per year between 1992 and 1997, says Freedonia. It recently predicted a 1.6% per year decline in overall solvent demand by volume through 1997, falling from the 1992 level of 12.6 billion lb per year. But much of the major reformulations and process changes are already under way, says Freedonia; the 1987–92 period saw a steeper decline of 5.1% per year.

Many traditional solvents are on environmental "hit lists." Of the three main types of solvents—hydrocarbons, chlorinated hydrocarbons, and oxygenates—chlorinated solvents are facing the biggest challenges. Ozone depleters 1,1,1-trichloroethane and chlorofluorocarbon (CFC)-113 are nearing a Jan. 1, 1996, production and import ban under the Montreal Protocol on Substances That Deplete the Ozone Layer. Meanwhile, chlorinated solvents are under the general pressure all chlorinated products face, says SRI International senior consultant Eric Linak, referring to recent calls for banning use of chlorinated compounds.

Moreover, highly volatile organic compounds—smog precursors—have been removed from many applications and products because of strict California requirements.

Less onerous but more broadly applicable is the Environmental Protection Agency's TRI and 33-50 program, which calls for voluntary emission reductions of 17 chemicals, including six commonly used solvents. The 33-50 program is so named because companies agreed to reduce releases of the 17 listed chemicals 33% by 1992 and 50% by 1995, measured against 1988 TRI data. EPA says that in 1992, its 33% goal was surpassed, with companies achieving a 40% cut. Meanwhile, solvents on the 1990 Clean Air Act hazardous air pollutants (HAP) lists are already seeing a downward trend in demand, with new regulations scheduled for promulgation over the next six years.

Health concerns plague some solvents, such as monomethyl and monoethyl ethers and their acetates, blamed for high miscarriage rates among semiconductor industry workers.

As perchloroethylene use is reduced, dry cleaning may get wetter

Solvents are, by definition, the cornerstone of the dry cleaning industry, which is made up of 25,000 facilities in the U.S.

The industry is one of the major users of perchloroethylene, a suspected carcinogen and hazardous air pollutant, and the first industry to be regulated under the 1990 Clean Air Act's national emission standards for hazardous air pollutants (NESHAP).

In a partnership with cleaners and solvent makers, the Environmental Protection Agency has established a goal to reduce perchloroethylene emissions from the industry. Under EPA's Design for the Environment program, approaches range from tightening process operations to eliminating organic solvents with water-based "wet" cleaning methods.

Last year, EPA employees donated their dirty laundry to test the new multiprocess water and steam cleaning technology. Wearers rated the wet cleaning slightly preferable to standard dry cleaning, says EPA economist Ohad Jehassi, who helps coordinate the partnership. He warns that long-term results are as yet unknown. Two wet cleaners have since opened in New York City.

Multiprocess wet cleaning includes steaming out stains, pressing, and using soaps. Machine wet cleaning with washer extractors can be added to cut the amount of human labor. Microwave drying helps prevent shrinkage of wet-processed items.

The partnership is also examining supercritical carbon dioxide, which cleans under extremely high pressures, at very high costs. Other options include ultrasonic cleaning, hydrochlorofluorocarbons and hydrofluorocarbons, and the return of mineral spirits in new nitrogen-purged machines to reduce fire hazards. EPA is also considering an environmental certification program for dry cleaners.

Perchloroethylene was a miracle replacement for the flammable—and explosive—petroleum solvents of the early 1900s. Mineral spirits and ozone-depleting chlorofluorocarbon-113 continue to be used, but at low levels.

Cleaners have always recycled solvents through filtering and reuse, says William Fisher, International Fabricare Institute senior vice president for government relations and administration. And when perchloroethylene became subject to all the regulations for hazardous wastes, cleaners had to send still bottoms—the molasseslike dirt-filled solvent—to recyclers or incinerators.

Perchloroethylene use has already been cut by careful housekeeping and improved machines. Sales to the industry in 1993 fell 27% from 1986 to 200 million lb. In 1975, says Center for Emissions Control executive director Steve Risotto, the average "solvent mileage" was 8,000 lb of clothes per 55-gal drum of perchloroethylene. In 1993, the same amount of the chemical cleaned 16,000 lb of clothing.

In September 1993, dry cleaners received final regulations under the Clean Air Act's NESHAP program. The requirements, to be fully implemented by 1996, call for better work practices and record keeping, a fugitive emission prevention program, regular filter changes, and checks for leaks. Larger and new facilities must install refrigerated condensers to control process vent emissions. EPA says the move will cut emissions of perchloroethylene 37% from current levels of 96,200 tons, with 7,300 tons cut through captured vent emissions and 28,400 tons eliminated through leak detection and repair.

In addition, dry cleaners will no longer be permitted to purchase "transfer" machines. Transfer machines, which account for 25% of those in use, were the first dry cleaners. Essentially a separate washer and dryer, transfer machines allow much solvent to evaporate during the transfer of clothes. Newer dry-to-dry machines vent to absorbers or refrigerator condensers. Some evacuate the drum before the door is opened.

Fisher cites problems with many of the alternatives, such as the high pressure and cost of supercritical carbon dioxide and the possibility of damage to very delicate fibers from ultrasonics.

Although he doesn't want a rushed decision to eliminate perchloroethylene, it's a decision the dry cleaning industry would learn to live with. "We're a service industry," says Fisher. "We're not married to 'perc.'"

But where there are losers, there are winners. With the phaseout of ozone-depleting compounds, says Chem Systems vice president Larry Rosenberg, "a wide range of alternative products—[such as] aqueous blends, oxygenates, terpenes, *N*-methyl-2-pyrrolidone—are vying for market share." Because there is as yet no exact drop-in replacement, he says, the "range of suppliers is also diverse, including traditional solvents producers and numerous formulators."

Although use of ethylene glycol ethers is declining, demand for propylene glycol ethers is projected to grow. Similarly, although demand for the HAP-listed ketones, such as methyl ethyl ketone and methyl isobutyl ketone, will likely decline, use of the small-volume, nonlisted methyl isopropyl ketone and methyl amyl ketone probably will expand, says Shomik Majumdar, Frost & Sullivan industry analyst. Esters, with a clean bill of environmental health, "are definitely going to grow," he says, perhaps at 3 to 4% per year. Ethyl acetate could replace ketones, and *n*-butyl acetate, as well as isopropyl and *n*-propyl acetate, should also grow. The real winners, he adds, may be hybrid aqueous-nonaqueous solvents.

Users and producers are finding new solvent combinations and applications for low-use solvents. Almost everything used to be cleaned with CFC-113 or 1,1,1-trichloroethane, says Michael Hayes, vice president of technology at Petroferm, Fernandina Beach, Fla. Petroferm now has two solvent replacement lines, one based on the citrus-peel-derived terpene *d*-limonene and tropical-oil-derived esters, the other based on aliphatic and cycloaliphatic hydrocarbons.

ISP "engineered" solvents to replace environmentally harmful cleaners, degreasers, and paint strippers. Its six products are very specialized, niche-oriented, says Bianca Thayer, market development specialist for ISP. The firm has expanded its sales force to seven, and is adding a product to the line later this year. The products, based on *N*-methyl-2-pyrrolidone, γ-butyrolactone, and dipropylene glycol monomethyl ether, also include additives such as rust inhibitors and surfactants.

However, customers "have to change the way [they] clean," says Thayer. Most must abandon the vapor degreaser—a one-step process—for a dip-tank rinse and dry operation.

"There are so many alternatives now," says Jeff Dore, Ashland Chemical's business manager for the cleaning alternatives unit. "The customers are being forced to make decisions" and trade-offs, he says. "Before, the chemistry made the decision for them." Vapor degreasing, the traditional method of metal and electronics parts cleaning, says Dore, "is going to become extinct."

In vapor degreasing, quick evaporation was an asset, but with the new cleaners, low volatility is key. Recycling and reuse of cleaners means that a new, higher priced product can be less expensive in the long run. A company that would require 100 drums of 1,1,1-trichloroethane may need only 35 to 50 drums of a replacement, says Dore.

Only 20 to 30% of Ashland's customers are in the process of changing from 1,1,1-trichloroethane, despite the January 1996 phaseout goal. Since all the alternatives have trade-offs, Dore says most users, particularly those with small operations, are reluctant to gamble on less than perfect replacement chemistry or new capital equipment before the deadline. Also, an alternative may become the target of new regulations. "They want a permanent solution," says Dore.

Ashland has blended seven alternatives to 1,1,1-trichloroethane. Introduced two years ago, they are based on hydrocarbon solvents and glycol ethers. Ashland is also beefing up its technology staff. "It's a different sell from what our [salespeople] are used to," Dore says. "We've gotten into a more specialized area that requires more of a technical sell, more technical assistance."

Customers may also be holding out for hydrofluorocarbons (HFCs). They will be very expensive, he says, but come closest to a drop-in replacement. DuPont expects to conclude toxicity testing on its HFC product 43-10 by the end of this year.

"We're hoping that it will turn out to be a big market, with a variety of applications," says Del Glover, DuPont vice president and global business director of fluorochemical cleaning agents. DuPont is pinning much of its hopes on 43-10 and other HFCs as replacements for CFC-113. DuPont may commercialize the product by the beginning of 1995.

For the transitional period, DuPont is selling perfluorocarbon solvents to a "very limited" market of customers—mainly in the military and aerospace industries. Customers ensure tight environmental controls on the solvent, suspected to be a major contributor to global warming.

Some have said that "growth and solvents are oxymorons," says Nigel Bell, Shell Chemical's business manager for solvents. "We have found that that is very much not the case." Shell, the largest solvents maker both in the U.S. and worldwide, has been increasing production at its solvents plants and has spent "several million dollars for rejuvenation" of its isopropyl alcohol plant in Deer Park, Tex.

Bell sees opportunities in replacement solvents and in the export market. For example, use of ketones is declining in the U.S. because they are included on the hazardous air pollutants list, but use is growing outside the U.S. Methyl ethyl ketone and methyl isobutyl ketone "are being embraced because they allow you to get aromatics out of paints," says Bell.

Environmental regulations have changed the way Shell views the solvents market. Only four or five years ago, solvents were a commodity market with price the main difference between suppliers. Now, producers must understand how their customers are using solvents. Shell has increased its marketing staff and increased research efforts over the past two years to respond to the changes.

The company has invested heavily in developing an "enormous" capacity in "hydrotreated" solvents at its Deer Park and Sarnia, Ontario, plants. Hydrocarbons are processed to remove aromatics, olefins, and sulfur, yielding low-odor, low-aromatic-level products.

Shell is also working with Ashland Chemical to market its diacetone alcohol shipbuilding cleaner to replace acetone. The alcohol has a lower flash point and one tenth the volatility of acetone, so it should be safer and last longer.

In addition, the cleaner is sold as part of a complete chemical service. Customers purchase the solvent, then return the exhausted product to Ashland to recycle it. Says Bell: "It's a trend that will develop more and more in the solvents business."

Dow Chemical, with a portfolio that leans heavily on the shaky chlorinated hydrocarbons, is restructuring its chlorinated solvents business. Dow has invested $100 million over the past three years in "sorting out our future [and getting the business] reconfigured and sized right," says senior product manager Jeff Sullivan. In April, Dow built up inventory to fill demand to the end of 1995, then shuttered its 500 million-lb-per-year 1,1,1-trichloroethane unit in Freeport, Tex.

In Stade, Germany, Dow is converting its 220 million-lb-per-year 1,1,1-trichloroethane plant to produce trichloroethylene (TCE), which has a future as a feedstock for HFC-134a. The conversion is to be completed by the end of this year.

At both Plaquemine, La., and Stade, Dow is pushing its perchloroethylene-

Decline in solvents use to continue at about 1.6% a year

Millions of lb	1987	1992	1997	% annual change 1987–92	% annual change 1992–97
BY TYPE					
Hydrocarbon solvents	8,282	4,735	4,000	–10.6%	–3.3%
Alcohols, esters, ethers	3,624	4,182	4,563	2.9	1.2
Chlorinated solvents	1,998	1,393	688	–7.0	–13.2
Ketone solvents	1,294	1,177	1,137	–1.9	–0.7
Glycols, esters, ethers	921	811	862	–2.5	1.2
Other	222	273	339	4.2	4.2
BY MARKET					
Coatings, printing inks, adhesives	10,081	6,826	6,091	–7.5	–2.3
Consumer markets	2,656	2,647	2,804	–0.1	1.2
Manufacturing & process	1,259	1,271	1,315	0.2	0.7
Industrial cleaning	1,481	1,112	672	–5.6	–9.6
Miscellaneous	864	715	707	–3.7	–0.2
TOTAL USE	16,341	12,571	11,589	–5.1%	–1.6%
TOTAL VALUE ($ billions)	$3.34	$2.85	$2.97	–3.2%	0.8%
AVERAGE VALUE (cents per lb)	20.5	22.7	25.6	—	—

Source: Freedonia Group

New programs help industry smooth the transition away from solvents

Solvent users don't have to go it alone. Almost every producer has a program to help users of embattled solvents switch to a new formulation or process. Dow Chemical has made a business of its Advanced Cleaning Systems program, and many other makers have computerized assistance to help find the best match for a working—but soon to be obsolete—paint formulation.

Dow Chemical's Advanced Cleaning Systems began in 1991 to help customers survive the phaseout of chlorofluorocarbon (CFC)-113 and 1,1,1-trichloroethane under the Montreal Protocol on Substances That Deplete the Ozone Layer and the Clean Air Act. 1,1,1-Trichloroethane "was by far the most used, easiest, and efficient cleaning solvent," eulogizes marketing communications manager Jon Kirst. "It is a very efficient molecule, the vapor is able to separate soil from a part without harming the part, there's no impingement, no distortion. It liked grease and oil. There really isn't an apples to apples replacement for it."

The best replacement depends on the item to be cleaned: A complicated multidimensional surface is harder to clean, and there are different levels of clean. For aerospace and medical uses, Kirst says, "it better be very clean." He says the company is completely independent from Dow's solvent sales: Advanced Cleaning Systems has directed some users to aqueous systems, others to solvents that can be used in a vapor degreaser system, and others to no-clean fluxes.

Kirst plans to continue the business beyond the January 1996 deadline to phase out ozone depleters. "We're already looking at other things we can offer," such as handling wastewater and volatile organic compounds.

Most major solvent suppliers offer computerized conversion assistance, says Ron Litton, principal technical representative and supervisor of the coating laboratory for Eastman Chemical. The programs are primarily for paint reformulations, but can help in developing cleaning solutions, too. Computerization has brought the response time down to days instead of weeks, or even just a few hours. "It depends on the complexity," he explains.

The programs were developed years ago for cost and performance improvements, or to deal with the shortage of a particular product. The programs can be fairly sophisticated, says Thomas Boyce, Dow Chemical's oxygenated solvents research leader. Dow's program contains a database of physical properties, such as flashpoints, thermodynamic functions, vapor pressure, and hazard evaluations.

"Now with the environmental issue, many requests are dictated by that," says Litton. Over the past five years, Eastman has added environmental models, tagging solvents with regulations that may limit their use. Reformulation—and use of the systems—has picked up over the past five years.

Water has also been added to databases as a solvent option. "The biggest difficulty in adding aqueous solutions is relative humidity," says Litton. Water doesn't handle the same way under different relative humidity levels. Organic solvents, on the other hand, tend not to be affected as much by humidity.

Chlorinated compounds, because of their low flammability, are difficult to replace. For aromatics, the user can combine oxygenated hydrocarbons and aliphatics to mimic toluene or xylene. "The likelihood of a one-for-one replacement is less than 10%," says Litton, "and nine times out of 10, the costs will rise."

The program at Eastman was written by chemists with some computer training. To begin, a user enters the current formula and the new requirements. The computer then calculates key parameters, and finds other combinations that match those parameters. "We focus on solubility constants and evaporation rates. If we can match those two parameters, we are a long way to our goal," Litton says.

But that's as far as the program will help. Then an experienced chemist will examine the computer's recommendations and eliminate obvious problems, such as flammable acetone for a use that would be compromised by flammability. Laboratory tests of promising mixes might follow.

"It really takes someone with application experience to sit down and have a look at [the results]," says Hoechst Celanese staff applications chemist Donald Raff. "Computers just spit out numbers. Some of this is an art."

carbon tetrachloride "swing" plants to 100% perchloroethylene production through hardware modifications, repiping, and altered process conditions. Nearly 98% of carbon tetrachloride is used as a feedstock for ozone depleters CFC-11 and CFC-12, which are scheduled for phaseout at the end of 1995. Carbon tetrachloride has suffered reduced use as a solvent because of toxicity concerns, says Sullivan, although it is still used as a cleaning solvent "in very closed conditions."

Despite perchloroethylene's future as a feedstock for HFC-134a, overall use has dropped because of changes in the dry cleaning industry and phaseout of ozone depleter CFC-113, for which perchloroethylene is a feedstock. Dow's Aratu, Brazil, perchloroethylene-carbon tetrachloride plant will stop production this summer. In 1992, Dow shuttered its Sarnia plant. Its plant in Pittsburg, Calif., closed in 1991.

Meanwhile, Dow has expanded capacity for chloromethanes. Its Plaquemine plant, operational at the end of 1993 after process improvements, is now producing methyl chloride, methylene chloride, and chloroform. The company also slightly increased chloroform production at its Freeport plant, following an increase in demand for chloroform as a feedstock for hydrochlorofluorocarbon (HCFC)-22.

"People are going to take the worst solvents out first, and the best ones are those that are remaining," says Fred Schillinger, business director for solvents and intermediates for Union Carbide. "As the other solvents are reduced, oxygenated solvents make up some of the difference."

And Carbide's oxygenated solvents portfolio, according to Freedonia Group, is already the largest in the U.S. In 1992, Carbide had $237 million in sales of alcohols and esters, $76 million in glycol ethers, and $25 million in ketones, Freedonia says. A Carbide spokesman says those numbers are low.

The company is increasing capacity for its oxo alcohol and butanol area, with a 300 million-lb-per-year expansion due on stream in January 1996 at its Taft, La., plant. "Solvents like alcohols—including butanol—and solvents like esters—butyl

acetate or isobutyl acetate, which are derivatives of butanol—are not under the same kind of pressure [because] they're not on a HAP list or a [TRI] list." Schillinger says demand is growing for butanol and butyl acrylate—which are used in water-based paints—at 4% per year. Carbide introduced specialty solvents based on ethyl 3-ethoxy-propionate and on butyl propionate and pentyl propionate a few years ago.

Glycol ethers that have not been implicated in causing health problems have been tarred by EPA's broad brush, says Schillinger. EPA's HAP list includes glycol ethers, not specifically the ethylene-based versions implicated in increased miscarriages. Glycol ethers "could be hurt if they stay on the list," he says.

In March, Carbide expanded its butyl glycol ether facility at Seadrift, Tex., by 80 million lb to 240 million lb a year and will continue methyl glycol ether production at its Taft plant to supply the jet fuel market, although the semiconductor market has been lost because of health concerns. The company is also repositioning and repricing its specialty solvent hexyl glycol ether to encourage use. "We hope it can grow substantially," he says, although it will "never be a 100 million lb product."

Monsanto is starting up a dimethyl ester line at its Pensacola, Fla., plant at the end of this month or early in July. "This stuff's fairly benign in the world of solvents," says Gary Winfield, Monsanto's market development manager for specialty resins. "There are no known health effects, [and the solvents are] readily biodegradable in five to seven days."

The move also cuts Monsanto's waste disposal costs, since raw material for the dibasic esters is harvested from the waste stream of its adipic acid unit. The acid waste is then converted and purified. Monsanto is developing six products from three coproduced esters—dimethyl glutarate, dimethyl succinate, and dimethyl adipate. With a total capacity of 20 million lb a year, the six products include the pure esters and blends that compete with DuPont's series.

DuPont has tapped its adipic acid line for dibasic esters for nearly two decades, says DuPont's product development manager, Lisa Boothe. The esters can be used for cleaning or as carriers in paints and coatings, with the "added value" of low toxicity and low volatility. There's been steady growth for the dibasic esters over the past five years, she says, with anticipated growth of 5 to 6% over the next few years. DuPont's adipic acid plant in Singapore, due on stream next year, will yield a large new source for the company. Monsanto's gambit, she says "reaffirms market growth for dibasic esters."

Exxon has focused attention on its specialty solvent product lines. It is betting on aliphatic isoparaffins and normal paraffins, as well as heavy aromatics and dearomatized aliphatic hydrocarbons. Says Ross Shirkey, Exxon's sector planner for differentiated hydrocarbons, the isoparaffins' narrow boiling ranges optimize formulations, and the dearomatized aliphatics promise low toxicity and reduced odor.

However, Exxon is not cutting back production of the traditional hydrocarbon solvents. "Very often [replacements] are not drop-in solutions," says Shirkey. There is "a certain amount of inertia" keeping customers from changing, and many are waiting to see how the alternatives shake out. "We'll see more and more converting as customers see their competition going to safer value-added products," says Shirkey.

Eastman Chemical is also continuing production of traditional solvents at the same level, says Eric DeLoach, business manager of coatings, inks, and resins. Some of the government regulations under the Clean Air Act aren't due to take effect until after 2000, he explains, so formulators have five to 10 years until the regulations actually go into force.

That's not to say that Eastman hasn't put its hat into the alternatives ring. Eastman entered the specialty solvents market in the 1960s to 1970s with methyl amyl ketone and methyl propyl ketone. And as paint and coating mixes move toward water-based solvents, the company's ester alcohol finds a place as a coalescing aid and the ethylene glycol monobutyl ether finds a place as a coupling solvent in the mix.

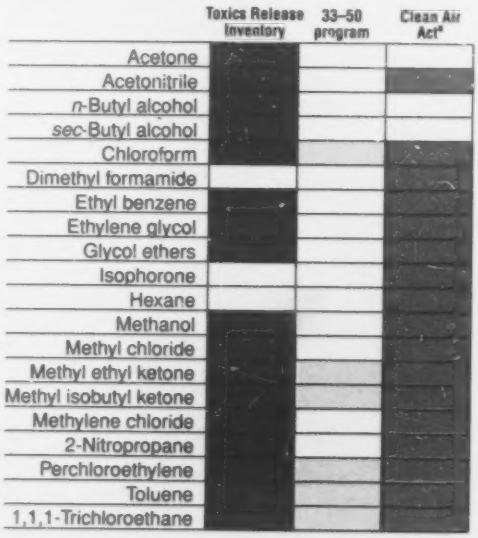
Environmental concerns have been a mixed blessing for Hoechst Celanese's acetate esters and acetic ester solvents, says Ken Stelts, marketing manager of the solvents business group. Methyl ethyl ketone and methyl isobutyl ketone were affected the most, declining 3% per year. "On the positive side, acetate esters are not listed [as HAPs]. They are benefiting as substitutes for toluene, xylene, and ketones," growing at 4 to 5% per year.

Late last year, Hoechst Celanese announced a process improvement initiative to increase production of acetate esters 25%. "I think we have some further options," Stelts adds.

Hoechst Celanese is also betting on Methylal, its methylene dimethyl ether specialty solvent. Now used primarily as an intermediate in the manufacture of ion exchange resins and as an extraction solvent for pharmaceuticals, Methylal could replace chlorinated solvents or be a cosolvent in aqueous systems, he says.

For users, a hierarchy of environmental concerns drives solvent choice, says John Carberry, DuPont's director of process and environmental research and development. "We concentrate on what should be attacked, from acutely toxic ones, such as benzene and methylene chloride," to ozone depleters, flammables, global-warming compounds, smog precursors,

Most common solvents are included in regulatory listings



[a] Hazardous air pollutants listing.
Sources: Hoechst Celanese, Eastman Chemical, EPA

Receive hands-on experience in DNA isolation, digestion with restriction enzymes, and isolation and separation by agarose gel electrophoresis.

Recombinant DNA for Chemists

THURSDAY–FRIDAY, AUGUST 18–19, 1994
GEORGETOWN UNIVERSITY • WASHINGTON, D.C.

A Dynamic Short Course Presented by the American Chemical Society in conjunction with the ACS 208th National Meeting

THIS COURSE FEATURES

- An overview of DNA replication, transcription, and translation
- Transformation of bacterial cells with recombinant DNA
- General strategies for cloning, selecting recombinant DNA plasmids, and analyzing recombinant DNA plasmids using restriction enzymes

Register Today!

Space is limited and enrollment is on a first-come, first-served basis.

For more information, call the ACS Continuing Education Short Course Office at (800) 227-5558 or (202) 872-4508. Or mail or FAX the coupon below.

YES! Please send me information on *Recombinant DNA for Chemists* to be held Thursday–Friday, August 18–19, 1994 in conjunction with the 208th ACS National Meeting in Washington, D.C.

Name _____

Title _____

Organization _____

Address _____

City, State, Zip _____

FAX _____

Mail to: **American Chemical Society,** Dept. of Continuing Education, Meeting Code ACS9408, 1155 Sixteenth Street, N.W., Washington, D.C. 20036.

FAX to: **(202) 872-6336**

and chemicals that create oxygen demand in wastewater.

Carberry says as many as 70% of DuPont's businesses use a solvent, and the company is examining them for opportunities to reduce the number or amount used. "The best solvent is no solvent at all," he says, an attainable goal in some projects. Coating and casting operations are going to high-temperature no-solvent melts, but with some concern about thermal degradation. Water is the next preferred solvent, with gains in surfactant research in the 1960s and 1970s making aqueous solutions more effective. "Unfortunately," says Carberry, "in the chemical industry, water is not a good solvent."

Cleaning solvents are the easiest to change or eliminate, he explains. Less frequent cleaning, solvent recovery systems, and high-pressure water sprays can cut solvent use.

Solvents in process reactions, on the other hand, are more difficult to alter. "You're talking big money," he says. "Most [process solvents] influence the character of the product," such as the crystal shape. When a change is necessary, DuPont frequently opts for a flammable solvent as the least of the environmental evils. But that necessitates multimillion-dollar expenditures to prevent explosions, says Carberry.

Process solvents are highly proprietary, he adds, with most companies "working very, very hard" to find new formulations. Other options for preventing health or environmental problems include sealed systems and remote operations.

Since the 1970s, 3M has been moving away from solvent-based coatings on its products, which include adhesive tapes, abrasive papers, computer diskettes, and video cassettes. "We make about 60,000 different products," says Robert Bringer, staff vice president for environmental engineering and pollution control. "Three quarters [of them] have a coating operation."

With 20% of its R&D funding aimed at cleaner technologies, 3M has now converted about 25% of the processes to aqueous and nonsolvent technologies. The earliest changeovers were adhesive tape and packaging tape. Multilayer coatings are the most difficult, says Bringer, because each layer must be compatible with the others. Videotapes present a special challenge. "Magnetic recordings are gaining by leaps and bounds in terms of

density of recording area, requiring thinner and thinner coatings. That goes against the grain when you are [trying to eliminate] solvents."

In addition to the phaseout of two of its cleaning fluids, the semiconductor industry has also been grappling with the ethylene-based glycol ethers. Studies have linked their use to an increased rate of miscarriages among industry workers. In December 1992, after the Semiconductor Industry Association (SIA) completed a health study that corroborated other research, most members agreed to phase out the use by the first quarter of 1995. Possible replacements, says SIA director of environmental and safety affairs Lee Neal, include ethyl lactates and propylene-based glycol ethers.

Because of military specifications, not all users will abandon the solvent, but "the days of ethylene-based glycol ethers in this industry are numbered." Neal—who says only 2.5% of the use is in the semiconductor industry—is pressing for reductions of ethylene glycol ethers throughout industry.

In the personal care business, "Everybody is looking for safe solvents," says Martin Rieger, a consultant to the Cosmetics, Toiletries & Fragrances Association.

Toluene has been pushed out of many nail polish formulations because of toxicity concerns and challenges based on carcinogen labeling required by California's Proposition 65, a ballot initiative passed in the state several years ago. Anecdotes of water-based nail polishes abound, in which unnamed companies were thrilled with results—until the tester washed her hands.

Rieger says water-based formulations with surfactants lose efficacy, but some activity can be restored with propylene glycol. For perfumes, he says, "you simply cannot make a clear product without alcohol." Deodorants long ago evolved from aerosol sprays, and the market is heavily represented by solids.

Water is beginning to live up to its title as "the universal solvent" throughout industry. Aqueous-based products are taking over much of the market for cleaning parts and equipment. And new surfactant and emulsion technologies are advancing water-based coatings and adhesives.

Cleaning out reaction vessels in batch processes is one high-volume use for solvents that is a target for aqueous re-

The Power to Deliver

COMPOUNDS

Quantities

Available in commercial quantities

To Order

SAF's broad range of chiral compounds are manufactured to ensure you of quality and consistency in every lot. To order or to receive a FREE SAF Brochure, Please contact us:

TEL: 800-336-9719

FAX: 800-368-4661

SAF BULK CHEMICALS

(the power of three)^3™

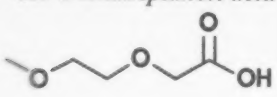
Sigma, Aldrich, Fluka Chemical Companies

CIRCLE 11 ON READER SERVICE CARD

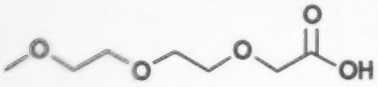
Hoechst offers out of R+D:

Oxa acids

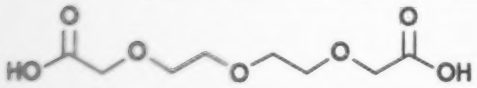
3.6-Dioxaheptanoic acid



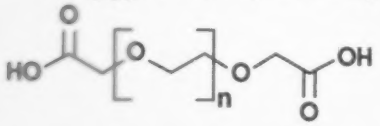
3.6.9-Trioxadecanoic acid



3.6.9-Trioxaundecanedioic acid



Polyglycol diacid (n = 10 - 12)



another example of Hoechst High Chem

Ask for our brochure!

Hoechst Celanese Corp.
Fine Chemicals Division
P.O. Box 1026
Charlotte, NC 28 201-1026
USA
Fax 704-559-6153
Phone 800-242-6222 ext. 6183

Hoechst AG
Marketing Feinchemikalien/CTM
D-65296 Frankfurt am Main
Germany
Fax (69) 3 05-1 64 26
Phone (69) 3 05-1 36 57
or 3 05-67 29

Hoechst Celanese
Hoechst

0027/C&EN

CIRCLE 14 ON READER SERVICE CARD

Your Key To Innovation:
Fine Chemicals From Eastman

DIETHOXYMETHANE

$H_3CCH_2OCH_2OCH_2CH_3$

- A cost-effective replacement for glyme.
- Stable under basic conditions.
- Does not require drying for use in organometallic reactions.
- Used as a solvent to prepare Grignard reagents.
- Useful as process and extraction solvent due to its low boiling point and low water miscibility.
- Useful as ethoxymethyl protecting group for alcohols, phenols and amines.
- Useful solvent in non-aqueous batteries and as fuel additives.
- Commercial quantities available immediately.

National Quality Award 1993 Winner
Eastman Chemical Company

EASTMAN
The Chemistry of New Ideas

For more information, please contact Sherry Wells at 1-800-EASTMAN or (615) 229-1480; Fax: (615) 229-8133. Or write to Eastman Chemical Company, Fine Chemicals, PO Box 431, Kingsport, TN 37662.

© Eastman Chemical Company
Eastman produces chemicals, not finished products, and therefore makes no warranties with respect to such products.

CIRCLE 21 ON READER SERVICE CARD

placements. Solvents are a part of Monsanto's pollution prevention effort. Of the 57 million lb of emissions reduced between 1987 and 1992, says Monsanto director of regulatory management Dennis Redington, 10% would normally be classified as solvents.

Pharmaceutical operations, he says, need to be cleaned to less than parts-per-million contamination. In switching to high-pressure water for some of the applications, Redington says Monsanto has cut air emissions 87%, wastewater discharges 71%, and costs by $500,000 per year. Monsanto also found ways to recycle and reuse 600,000 gal per year of waste solvents from manufacturing.

Many agricultural chemicals depend on solvents to mobilize reactants. Monsanto managed to move from chlorobenzene to water in the Lasso corn and bean herbicide formulation. The difficulty, he says, is getting active ingredients into small particles for emulsion. The production process keeps a careful eye on density control, using suspending agents to keep particles from settling, which extends the shelf life.

California's South Coast Air Quality Management District (SCAQMD) has waged "virtually an all-out full-scale attack" on emissions of VOCs, says Larry Watkins, SCAQMD's program supervisor for economic development and business retention.

"We've been focusing on the end users," he says, adding that every manufacturer has complied, because southern California "is a big market."

The biggest new cleaners in the area are water and elbow grease. "Water works," says Watkins. "Water has been shown to work probably in 85 to 90% of processes and products." Using surfactants, emulsifiers, and mechanical cleaning, manufacturers have introduced thousands of aqueous formulations. It used to be, he says, that with a regular solvent based on VOCs, cleaning action was "90% chemical, 10% mechanical. Nowadays, cleaning is 90% mechanical."

Environmental and health concerns have changed the solvents industry—and downstream products—for good. Some of the qualities of the banned and embattled solvents may never be replicated by replacements. "The world is going to have to get used to the difference," says Monsanto's Winfield. Carbide's Schillinger agrees: "There's only so much you can do with chemistry." □